PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

NOVEMBER 2004 SAMPLING EVENT

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Pesticide Monitoring Project Report
November 2004 Sampling Event

Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 37 sites were collected from November 29 to December 2, 2004, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides ametryn, atrazine, hexazinone, metalaxyl, metolachlor, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, alpha endosulfan, beta endosulfan, and endosulfan sulfate were detected in one or more of these surface water samples. However, none of the concentrations exceeded numeric or calculated criteria.

The herbicides ametryn and atrazine, together with the insecticides/degradates aldrin, chlordane, DDD, DDE, DDT, dieldrin, alpha endosulfan, beta endosulfan, endosulfan sulfate, two PCB compounds, and toxaphene were found in the sediment at several locations. The toxaphene, chlordane, one DDD and three DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-seven pesticides and degradation products were analyzed for in samples from all of the 37 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application described herein, are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, or dermal uptake). Primary ground water standards are enforceable standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the United States Environmental Protection Agency (USEPA) under Section 304 (a) of the Clean Water Act, if available, or the lowest effective concentration (EC_{50}) or lethal concentration (LC_{50}) reported in the summarized literature. Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, LTD., and United States Geological Survey, 2003). A value below the threshold effects concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from November 29 to December 2, 2004.

Results

At least one pesticide was detected in surface water at 29 of the 37 sites and in sediment at 20 of the 35 sites. Sediment samples are not collected at GORDYRD and CR33.5T. Sites NSIDWC06 and NSIDWC07 were deleted after fourteen sampling events as part of the continuous monitoring network optimization process. Changes in pesticide product labeling resulted in less usage with a subsequent reduction in detection and therefore possible decline in environmental impacts. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The sediment DDD, chlordane and toxaphene concentrations at S2 and DDE concentrations at S2, S5A, and S6 were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

<u>Aldrin</u>: Aldrin is a non-systemic insecticide with contact, stomach, and respiratory action, used primarily to control soil insects. Its use and manufacture has been discontinued in the United States. Environmental fate and toxicity data in Tables 4 and 5 indicate that aldrin (1) is relatively toxic to mammals and fish; and (2) due to the large hydrophobicity of this compound, results in a significant bioaccumulation factor. Freshwater sediment quality assessment guidelines have not been developed for aldrin due to insufficient data. The only aldrin concentration detected was 11 micrograms per kilogram (μg/Kg) at S2. No surface water detections of aldrin were found.

<u>Ametryn</u>: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (μg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface

adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.010 to 0.037 µg/L. Using these criteria, these observed surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The only sediment concentration detected was 15 µg/Kg at S6. However, no freshwater sediment quality assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow (Verschueren, 1983). The draft ambient aquatic life water quality criteria identify a one-hour average concentration that does not exceed 1,500 µg/L more than once every three years on the average (USEPA, 2003). The atrazine surface water concentrations found in this sampling event at 22 of the 37 sampling locations, ranged from 0.012 to 0.82 µg/L. Using these criteria, these observed surface water levels should not have an acute or chronic detrimental impact on fish or invertebrates. Only a TEC level (0.30 µg/Kg) has been developed for atrazine concentrations in freshwater sediments. The detected sediment concentration of atrazine at S2 (10.2 µg/Kg) exceeds this value and it is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). The highest DAR value 0.6 suggests that considerable degradation of atrazine has occurred in the S178 basin. However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlordane (1) is moderately toxic to mammals and highly toxic to fish; and (2) has the potential for significant bioconcentration. Freshwater sediment quality assessment guidelines identified a TEC of 3.2 μg/Kg and PEC of 18 μg/Kg for chlordane. The detected sediment residue of 260 μg/Kg at S2 is at a concentration where harmful effects to sediment-dwelling organisms are frequently or always observed. While the use of this compound has been discontinued in recent years, its persistence and tendency to accumulate in sediments makes chlordane a compound of concern. Chlordane was not detected in the surface water.

DDD, DDE, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD sediment concentrations detected range from 5.9 to 80 μg/Kg. Any concentration which would fall below the TEC (4.9 μg/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 μg/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentration detected at S2 (80 μg/Kg) exceeded the PEC. DDD was not detected in the surface water.

The TEC is 3.2 μg/Kg and the PEC is 31 μg/Kg for DDE in freshwater sediments. The concentrations of DDE detected at S2, S5A, and S6 exceed the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

The DDT concentration detected (59 μg/Kg at S2) exceeds the TEC (4.2 μg/Kg) but is less than the PEC (63 μg/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

Dieldrin: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. The high K_{oc} and low water solubility accounts for dieldrin's affinity for sediment. The hydrophobicity of this compound also results in a significant bioconcentration factor and the potential for a high degree of accumulation in aquatic organisms (Table 4). Dieldrin is highly toxic to mammals. The dieldrin concentration detected (20 μg/Kg at S2) exceeds the TEC (1.9 μg/Kg) but is less than the PEC (62 μg/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No dieldrin was detected in the surface water.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/Kg (Table 4). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). β endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 4). Endosulfan (α and/or β) was detected at five locations (S176, S177, S178, S18C, and S331) in the South Miami-Dade farming area (Table 2). However, these concentrations (α plus β) do not exceed the Florida Class III surface water quality standard (FAC 62-302). Although α and β endosulfan were detected in the sediment, no quality assessment guidelines have been developed.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Table 4). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The only surface water and sediment detections occurred at S178 (0.31 μg/L and 36 μg/Kg, respectively). However, no FDEP surface water standard (FAC 62-302) or sediment quality assessment guideline has been promulgated for endosulfan sulfate.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (USEPA, 1988). The highest surface water concentration detected in this sampling event at G94D (0.82 μg/L) should not have an acute impact on fish or aquatic invertebrates. No hexazinone was detected in the sediment.

Metalaxyl: Metalaxyl is a systemic fungicide. Registered uses include potatoes, strawberries, citrus, avocados and vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metalaxyl (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metalaxyl detected was 0.067 μg/L at GORDYRD (Table 2). Using these criteria, the concentrations of metalaxyl detected should not have an acute, harmful impact on fish or aquatic invertebrates. Metalaxyl was not detected in the sediment.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.22 μg/L at S178) is several orders of magnitude below the calculated chronic action level. Using these criteria, the observed level should not have a harmful impact on fish or aquatic invertebrates. No metolachlor was detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a LC_{50} of >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.032 to 0.44 μg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1242 and PCB-1254 are commercial grade mixtures containing 42 percent and 54 percent chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. Florida freshwater sediment quality assessment guidelines have been developed for total PCBs (MacDonald Environmental Sciences, LTD., and United States Geological Survey, 2003). The TEC and PEC are 60 μg/Kg and 680 μg/Kg, respectively, for total PCBs. Four sediment residues detected fall between the TEC and PEC (S79, S6, S31, and S7), which therefore have a possibility for impacting freshwater sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (USEPA, 1984). The only surface water concentration of simazine detected at S5A (0.024 μg/L) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Toxaphene: Toxaphene is an insecticide consisting of a complex mixture of polychlorinated camphene derivative containing 67 to 69 percent chlorine. As of November 1982 all products were cancelled. Environmental fate and toxicity data in Tables 4 and 5 indicate that toxaphene (1) is not easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and a small potential for loss due to surface solution; (2) is relatively toxic to mammals and fish; and (3) does not bioconcentrate significantly. This is only the second time toxaphene has been detected in the sediment since the formalized monitoring program was established in 1984. Freshwater sediment quality assessment guidelines identified a TEC and PEC of 0.01 and 32 μg/Kg, respectively for toxaphene. The residue detected at S2 (620 μg/Kg) exceeds the PEC and frequently or always has the possibility for impacting sediment-dwelling organisms. No toxaphene was detected in the surface water.

Quality Assurance Evaluation

Replicate samples were collected at sites S178, S2 and S5A. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No analytes were detected in the field blanks collected at S18C, S3, S12C, S191, S79, S190, and S6. No pesticide analytes were detected in the equipment blanks performed at S18C, S2, S3, S191, and S142. All collected samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. Table 7 lists parameters which did not meet the specified laboratory quality control requirements. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the USEPA with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

Glossary

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Method Detection Limits (MDLs):

The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs):

The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Threshold Effects Concentration (TEC):

The threshold effects concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

Probable Effects Concentration (PEC):

The probable effects concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

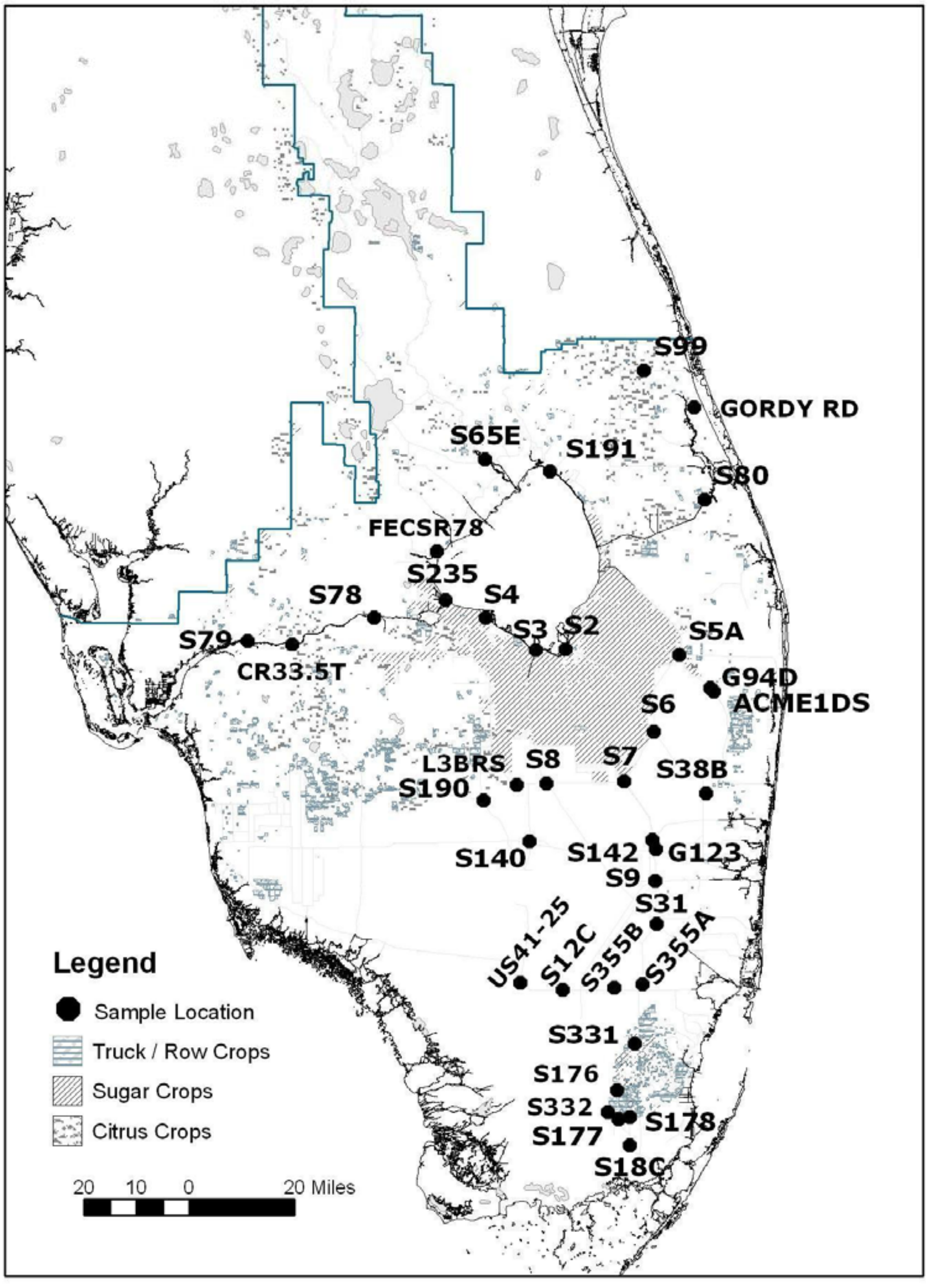

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for November 2004 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)
2,4-D	0.2 - 0.6	7.8 - 200	endosulfan sulfate	0.0045 - 0.056	0.78 - 27
2,4,5-T	0.2 - 0.6	7.8 - 200	endrin	0.0094 - 0.044	1.9 - 68
2,4,5-TP (silvex)	0.2 - 0.6	7.8 - 200	endrin aldehyde	0.0042 - 0.019	0.78 - 27
alachlor	0.047 - 0.22	23 - 800	ethion	0.019 - 0.088	1.9 - 68
aldrin	0.0019 - 0.0088	0.39 - 13	ethoprop	0.019 - 0.088	3.9 - 130
ametryn	0.0094 - 0.044	1.9 - 68	fenamiphos (nemacur)	0.028 - 0.13	16 - 520
atrazine	0.0094 - 0.048	1.9 - 68	fonofos (dyfonate)	0.019 - 0.088	3.9 - 130
atrazine desethyl	0.0094 - 0.044	N/A	heptachlor	0.0023 - 0.01	0.39 - 13
atrazine desisopropyl	0.0094 - 0.044	N/A	heptachlor epoxide	0.0019 - 0.0088	0.39 - 13
azinphos methyl (guthion)	0.019 - 0.088	1.9 - 68	hexazinone	0.019 - 0.15	7.8 - 270
α BHC (alpha)	0.0021 - 0.0096	0.39 - 13	imidacloprid	0.2 - 0.6	N/A
β BHC (beta)	0.0032 - 0.015	0.39 - 13	linuron	0.2 - 0.6	7.8 - 200
δ BHC (delta)	0.0019 - 0.016	0.78 - 27	malathion	0.028 - 0.13	5.8 - 200
γ BHC (gamma) (lindane)	0.0019 - 0.0088	0.39 - 13	metalaxyl	0.047 - 0.22	N/A
bromacil	0.038 - 0.17	16 - 520	methamidophos	N/A	19 - 680
butylate	0.019 - 0.088	N/A	methoxychlor	0.0098 - 0.044	9.7 - 330
carbophenothion (trithion)	0.015 - 0.068	1.9 - 68	metolachlor	0.057 - 0.26	19 - 680
chlordane	0.019 - 0.088	5.8 - 200	metribuzin	0.019 - 0.088	3.9 - 130
chlorothalonil	0.015 - 0.068	1.9 - 68	mevinphos	0.075 - 0.35	7.8 - 270
chlorpyrifos ethyl	0.019 - 0.088	1.9 - 68	mirex	0.011 - 0.052	1.6 - 52
chlorpyrifos methyl	0.0094 - 0.044	3.9 - 130	monocrotophos (azodrin)	N/A	19 - 680
cypermethrin	0.019 - 0.088	1.9 - 68	naled	0.075 - 0.35	32 - 1100
DDD-P,P'	0.0045 - 0.021	0.78 - 27	norflurazon	0.019 - 0.088	3.9 - 130
DDE-P,P'	0.0038 - 0.017	0.78 - 80	parathion ethyl	0.019 - 0.088	5.8 - 200
DDT-P,P'	0.0057 - 0.026	1.2 - 40	parathion methyl	0.019 - 0.088	5.8 - 200
demeton	0.11 - 0.52	39 - 1300	PCB	0.019 - 0.088	7.8 - 600
diazinon	0.019 - 0.088	3.9 - 130	permethrin	0.015 - 0.068	2.3 - 80
dicofol (kelthane)	0.042 - 0.19	5.8 - 200	phorate	0.028 - 0.13	1.9 - 68
dieldrin	0.0019 - 0.0088	0.39 - 13	prometryn	0.019 - 0.088	5.8 - 200
disulfoton	0.019 - 0.088	3.9 - 130	prometon	0.019 - 0.088	N/A
diuron	0.2 - 0.6	7.8 - 200	simazine	0.0094 - 0.044	1.9 - 68
α endosulfan (alpha)	0.0038 - 0.017	0.39 - 13	toxaphene	0.094 - 0.44	29 - 1000
β endosulfan (beta)	0.0038 - 0.017	0.39 - 13	trifluralin	0.0075 - 0.035	1.6 - 52
			zinc phosphate	0.5 - 2	N/A

N/A - not analyzed

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in November 2004.

Date	Site	Flow	ametryn	atrazine	atrazine desethyl	alpha endosulfan	beta endosulfan	endosulfan sulfate	hexazinone	metalaxyl	metolachlor	norflurazon	simazine	Number of compounds detected at site
11/29/2004	S176	N	-	-	-	0.0081 I	-	-	-	-	-	-	-	1
	S177	N	-	-	-	0.0052 I	-	-	0.021 I	-	-	-	-	2
	S178	N	-	0.025 I	0.012 I	0.025	0.019	0.31	-	-	0.22 I	-	-	6
	S18C	N	-	0.012 I	-	0.0084 I	-	-	-	-	-	-	-	2
	S2	N	-	0.084 *	0.023 I *	-	-	-	0.021 I*	-	-	-	-	3
	S3	N	-	0.096	0.029 I	-	-	-	-	-	-	-	-	2
	S331	Y	-	-	-	0.0047 I	-	-	-	-	-	-	-	1
	S332	N	-	-	-	-	-	-	-	-	-	-	-	0
	S4	N	0.032 I	0.060	-	-	-	-	0.043 I	-	-	-	-	3
11/30/2004	C25S99	N	-	-	-	-	-	-	0.14	-	-	0.29	-	2
	G123	N	0.010 I	0.016 I	-	-	-	-	-	-	-	-	-	2
	GORDYRD	Y	-	-	-	-	-	-	-	0.067 I	-	0.44	-	2
	S12C	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S191	N	-	-	-	-	-	-	-	-	-	-	-	0
	S31	Y	-	0.012 I	-	-	-	-	-	-	-	-	-	1
	S355A	N	-	-	-	-	-	-	-	-	-	-	-	0
	S355B	N	-	-	-	-	-	-	-	-	-	-	-	0
	S65E	Y	-	0.075	-	-	-	-	-	-	-	-	-	1
	S80	N	-	0.083	0.021 I	-	-	-	0.020 I	-	-	0.059 I	-	4
	S9	N	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	-	-	-	-	-	-	-	-	-	0
12/1/2004	CR33.5T	R	-	0.077	0.013 I	-	-	-	0.039 I	-	-	0.064 I	-	4
	FECSR78	N	-	-	-	-	-	-	-	-	-	-	-	0
	L3BRS	Y	-	0.0096 I	-	-	-	-	-	-	-	-	-	1
	S140	N	-	-	-	-	-	-	0.023 I	-	-	0.067 I	-	2
	S142	Y	0.011 I	0.015 I	-	-	-	-	-	-	-	-	-	2
	S190	Y	-	-	-	-	-	-	-	-	-	0.032 I	-	1
	S235	R	-	0.062	0.015 I	-	-	-	0.043 I	-	-	-	-	3
	S7	N	-	0.020 I	-	-	-	-	-	-	-	-	-	1
	S78	Y	-	0.10	0.020 I	-	-	-	-	-	-	-	-	2
	S79	Y	-	0.080	0.012 I	-	-	-	0.041 I	-	-	0.048 I	-	4
	S8	N	0.010 I	0.013 I	-	-	-	-	-	-	-	-	-	2
12/2/2004	ACME1DS	N	0.015 I	0.039	-	-	-	-	0.44	-	-	-	-	3
	G94D	N	0.010 I	0.073	-	-	-	-	0.82	-	-	-	-	3
	S38B	N	0.014 I	0.82	0.082	-	-	-	-	-	-	-	-	3
	S5A	Y	0.019 I *	0.19 *	0.026 I *	-	-	-	0.023 I *	-	-	-	0.024 I *	5
	S6	Y	0.037 I	0.012 I	-	-	-	-	-	-	-	-	-	2
Total number of compound detections			9	22	10	5	1	1	12	1	1	7	1	70

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitative limit, and greater than or equal to the method detection limit.

Table 3. Summary of pesticide residues (µg/Kg) above the method detection limit found in sediment samples collected by SFWMD in November 2004.

Date	Site	Flow	aldrin	ametryn	atrazine	chlordane	DDD-P,P'	DDE-P,P'	DDT-P,P'	dieldrin	alpha endosulfan	beta endosulfan	endosulfan sulfate	PCB-1242	PCB-1254	toxaphene	Number of compounds detected at site
11/29/2004	S177	N	-	-	-	-	-	5.4 I	-	-	-	-	-	-	-	-	1
	S178	N	-	-	-	-	-	26 *	-	-	14 *	10 *	36 *	-	-	-	4
	S18C	N	-	-	-	-	-	2.9 I	-	-	-	-	-	-	-	-	1
	S2	N	11 *	-	10.2 I *	***260 ****	***80 ****	***393 ****	59 *	20 *	-	-	-	-	-	***620 ****	8
	S3	N	-	-	-	-	5.9 I	21	-	-	-	-	-	-	-	-	2
	S331	Y	-	-	-	-	-	3.3 I	-	-	-	-	-	-	-	-	1
	S4	N	-	-	-	-	-	13 I	-	-	-	-	-	-	-	-	1
11/30/2004	G123	N	-	-	-	-	-	6.0 I	-	-	-	-	-	-	-	-	1
	S31	Y	-	-	-	-	-	2.2 I	-	-	-	-	-	77 I	-	-	2
	S80	N	-	-	-	-	-	8.4 I	-	-	-	-	-	-	-	-	1
12/1/2004	L3BRS	Y	-	-	-	-	-	3.2 I	-	-	-	-	-	-	-	-	1
	S142	Y	-	-	-	-	-	4.7 I	-	-	-	-	-	-	-	-	1
	S235	R	-	-	-	-	-	1.4 I	-	-	-	-	-	-	-	-	1
	S7	N	-	-	-	-	-	-	-	-	-	-	-	-	78	-	1
	S79	Y	-	-	-	-	-	10 I	-	-	-	-	-	-	66 I	-	2
	S8	N	-	-	-	-	-	1.9 I	-	-	-	-	-	-	-	-	1
12/2/2004	ACME1DS	N	-	-	-	-	-	1.6 I	-	-	-	-	-	-	-	-	1
	G94D	N	-	-	-	-	-	4.0	-	-	-	-	-	-	-	-	1
	S5A	Y	-	-	-	-	9.9	***36***	-	-	-	-	-	-	19 I	-	3
	S6	Y	-	15 I	-	-	24	***81***	-	-	-	-	-	-	75 I	-	4
Total number of compound detections			1	1	1	1	4	19	1	1	1	1	1	1	4	1	38

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitative limit, and greater than or equal to the method detection limit.
Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Table 4. Selected properties of pesticides found in November 2004 sampling event.

Common Name	Surface Water Standards FAC 62-302 (µg/L)	Ground Water Guidance Conc. (µg/L)	LD_{50} acute rats oral (mg/Kg) (1)	EPA Carcinogenic Potential	Water Solubility (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) Rating (2)			Volatility frrom Water	Bioconcentration Factor (BCF)
								LE	SA	SS		
aldrin	3	0.05	38-67	B2	0.05	48500	-	-	-	-	S	3348
ametryn	-	63	1110	D	185	300	60	M	M	M	I	33
atrazine	-	3**	3080	C	33	100	60	L	M	L	I	86
chlordane	0.0043	2**	365-590	B2	0.056	3800	-	-	-	-	I	3141
DDD, p,p'	-	0.1	3400	-	0.055	239900	-	-	-	-	I	3173
DDE, p,p'	-	0.1	880	-	0.065	243220	-	-	-	-	S	2887
DDT, p,p'	0.001	0.1	113	-	0.00335	140000	-	-	-	-	I	15377
dieldrin	0.0019	0.1	37 - 87	B2	0.14	10000 est.	-	-	-	-	I	1873
endosulfan alpha	0.056	0.35	70	-	0.53	12400	50	XS	L	M	S	884
endosulfan beta	-	0.35	70	-	0.28	-	-	-	-	-	S	1267
endosulfan sulfate	-	0.3	-	-	0.117	-	-	-	-	-	I	2073
hexazinone	-	231	1690	D	33000	54	90	L	M	M	I	2
metalaxyl	-	420	669	-	7100	100	70	L	M	M	I	4
metolachlor	-	1050	2780	C	530	200	90	L	M	M	I	18
norflurazon	-	280	9400	C	28	700	90	M	M	L	I	94
PCB's	0.014	0.5**	-	B2	-	-	-	-	-	-	-	-
simazine	-	4**	>5000	C	6.2	130	60	L	M	M	I	221
toxaphene	0.0002	3**	40 - 90	B2	3	100000	9	XS	M	S	-	333

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant
Bioconcentration Factor (BCF) calculated as BCF = $10^{(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP surface water standards (4/95) for Class III waters except Class I in ( )
Note: endosulfan considered the sum of alpha and beta isomers
** primary standard

(1) Hartley, D. and H. Kidd. (Eds.) (1987).
(2) Goss, D. and R. Wauchope. (Eds.) (1992).
(3) Montgomery, J.H. (1993).
(4) Lyman,W.J., W.F. Reehl, and D.H. Rosenblatt. (1990).
(5) United States Environmental Protection Agency (1996).

Table 5. Toxicity of pesticides found in the November 2004 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48-hr EC_{50} Water flea *Daphnia magna*		acute toxicity (*)	chronic toxicity (*)	96-hr LC_{50} Fathead Minnow (#) *Pimephales promelas*		acute toxicity	chronic toxicity	96-hr LC_{50} Bluegill *Lepomis macrochirus*		acute toxicity	chronic toxicity	96-hr LC_{50} Largemouth Bass *Micropterus salmoides*		acute toxicity	chronic toxicity	96-hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*		acute toxicity	chronic toxicity	96-hr LC_{50} Channel Catfish *Ictalurus punctatus*		acute toxicity	chronic toxicity
aldrin	-		-	-	28	(5)	9.3	1.4	13	(5)	4.3	0.65	-		-	-	17.7	(5)	5.9	0.89	-		-	-
ametryn	28,000	(7)	9333	1400	-		-	-	4,100	(4)	1367	205	-		-	-	8,800	(4)	2933	440	-		-	-
atrazine	6900	(7)	2300	345	15,000	(7)	5000	750	16,000	(4)	5333	800	-		-	-	8,800	(4)	2933	440	7,600	(4)	2533	380
chlordane	-		-	-	-		-	-	70	(5)	23	3.5			-	-	90	(5)	30	5			-	-
DDD, p,p'	3,200	(6)	1067	160	4,400	(1)	1467	220	42	(1)	14	2.1	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE, p,p'	-		-	-	-		-	-	240	(1)	80	12	-		-	-	32	(1)	10.7	1.6	-		-	-
DDT, p,p'	-		-	-	19	(5)	6.3	0.95	8	(5)	2.7	0.4	2	(5)	0.7	0.10	7	(5)	2.3	0.35	16	(5)	5.3	0.8
dieldrin	-		-	-	16	(5)	5.3	0.80	8	(4)	2.7	0.4	-		-	-	10	(5)	3.3	0.5	4.5	(5)	1.5	0.23
endosulfan	166	(7)	55	8	1	(1)	0.3	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(7)	0.5	0.08
	-		-	-	-		-	-	-		-	-	-		-	-	1	(3)	0.33	0.050	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	0.3	(5)	0.10	0.015	-		-	-
hexazinone	151,600	(7)	50533	7580	274,000	(4)	91333	13700	100,000	(7)	33333	5000	-		-	-	180,000	(7)	60000	9000	-		-	-
metalaxyl	28,000	(7)	9333	1400	-		-	-	139,000	(7)	46333	6950	-		-	-	132,000	(7)	44000	6600	-		-	-
metolachlor	23,500	(7)	7833	1175	-		-	-	15,000	(4)	5000	750	-		-	-	2,000	(4)	667	100	4,900	(5)	1633	245
norflurazon	15,000	(7)	5000	750	-		-	-	16,300	(7)	5433	815	-		-	-	8,100	(7)	2700	405	>200,000	(4)	>67,000	>10,000
simazine	1,100	(7)	367	55	100,000	(7)	33333	5000	90,000	(4)	30000	4500	-		-	-	100,000	(7)	33333	5000	-		-	-
toxaphene	-		-	-	-		-	-	-		-	-	-		-	-	200	(7)	67	10	-		-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson, W. W. and M.T. Finley (1980).
(2) U.S. Environmental Protection Agency (1977).
(3) Schneider, B.A. (Ed.) (1979).
(4) Hartley, D. and H. Kidd. (Eds.) (1987).
(5) Montgomery, J.H. (1993).
(6) Verschueren, K. (1983).
(7) United States Environmental Protection Agency (1991).

Table 6. Atrazine desethyl/atrazine ratio (DAR) data for November 2004 sampling event.

Date	Site	Flow	atrazine ug/L	moles/L	atrazine desethyl ug/L	moles/L	DAR
11/29/2004	S178	N	0.025	1.15910E-10	0.012	6.39551E-11	0.6
	S2	N	0.084	3.89457E-10	0.0233	1.2418E-10	0.3
	S3	N	0.096	4.45093E-10	0.029	1.54558E-10	0.3
11/30/2004	S80	N	0.083	3.84820E-10	0.021	1.11922E-10	0.3
12/1/2004	CR33.5T	R	0.077	3.57002E-10	0.013	6.92847E-11	0.2
	S235	R	0.062	2.87456E-10	0.015	7.99439E-11	0.3
	S78	Y	0.1	4.63639E-10	0.02	1.06592E-10	0.2
	S79	Y	0.08	3.70911E-10	0.012	6.39551E-11	0.2
12/2/2004	S38B	N	0.82	3.80184E-09	0.082	4.37027E-10	0.1
	S5A	Y	0.19	8.80914E-10	0.0263	1.40168E-10	0.2

DAR	All sites	Flow only sites	No flow sites
average	0.3	0.2	0.3
median	0.3	0.2	0.3
minimum	0.1	0.2	0.1
maximum	0.6	0.2	0.6

N - no flow; Y - flow; R - reverse

Table 7. Laboratory Quality Control Failures for November 2004 Sampling Event.

	Compound				
Site	chlorothalonil	2,4-D	mevinphos	azinphos methyl	dicofol
S176	MS–SD				
S177	MS–SD				
S178	MS–SD				
S178 RS	MS–SD				
S18C	MS–SD				
S331	MS–SD				
S332	MS–SD				
FECSR78			LCS-SD, MS-SD	LCS-SD	RPD-SD
S12C	MS–SD	MS–W			
S12C FB		MS–W			
S191	MS-SD				
S191 EB		MS-W			
S191 FB		MS-W			
S235			LCS-SD, MS-SD	LCS-SD	RPD-SD
S31	MS–SD	MS–W			
S355A		MS–W	LCS-SD, MS-SD	LCS-SD	RPD-SD
S355B		MS–W	LCS-SD, MS-SD	LCS-SD	
S65E	MS-SD	MS-W			
S78			LCS-SD, MS-SD	LCS-SD	RPD-SD
S79		MS-W	LCS-SD, MS-SD	LCS-SD	RPD-SD
S79 EB		MS-W			
S79 FB		MS-W			
S9		MS–W	LCS-SD, MS-SD	LCS-SD	RPD-SD
US41-25	MS-SD				
C25S99	MS-SD	MS–W			
G123		MS–W	LCS-SD, MS-SD	LCS-SD	RPD-SD
L3BRS		MS–W	LCS-SD, MS-SD	LCS-SD	RPD-SD
S140	MS–W		LCS-SD, MS-SD	LCS-SD	RPD-SD
S142	MS–W		LCS-SD, MS-SD	LCS-SD	RPD-SD
S142 EB	MS–W				
S190			LCS-SD, MS-SD	LCS-SD	RPD-SD
S190 FB		MS–W			
S2	MS-SD				
S2 RS	MS-SD				
S3	MS-SD				
S4	MS-SD				
S7			LCS-SD, MS-SD	LCS-SD	RPD-SD
S8		MS–W	LCS-SD, MS-SD	LCS-SD	RPD-SD
S80	MS-SD				
ACME1DS			LCS-SD, MS-SD	LCS-SD	RPD-SD
G94D			LCS-SD, MS-SD	LCS-SD	RPD-SD
S38B			LCS-SD, MS-SD	LCS-SD	RPD-SD
S5A			LCS-SD, MS-SD	LCS-SD	RPD-SD
S6			LCS-SD, MS-SD	LCS-SD	RPD-SD

MS: matrix spike; RPD: relative percent difference; RS: replicate sample; FB: field blank; EB: equipment blank; LCS: laboratory control sample; W: water; SD: sediment